

bonded to the N of the hydroxylamino group forms a hydrogen bond with the O of the coordinated water, the other with the O of the uranyl group. These last two hydrogen bonds are the weakest. The U—O distance of the uranyl group is rather longer than that normally observed, 1.75 Å, which is probably because of the hydrogen bonding. We have not found reports of a similar hydrogen bond. The N atoms form no hydrogen bonds.

We thank Dr G. Gafner of the Council for Scientific and Industrial Research for the loan of the Enraf-Nonius universal low-temperature device, and the Atomic Energy Board for permission to publish this paper.

*Acta Cryst.* (1977). B33, 3000–3003

## The Crystal and Molecular Structure of Tricarbonyl(2,5-dihydrothiophene 1-oxido)iron, $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_6\text{OS})$

BY F. A. J. J. VAN SANTVOORT, H. KRABBENDAM, G. ROELOFSEN AND A. L. SPEK\*

*Rijksuniversiteit Utrecht, Laboratorium voor Structuurchemie, Padualaan 8, Utrecht, The Netherlands*

(Received 14 February 1977; accepted 18 March 1977)

Tricarbonyl(2,5-dihydrothiophene 1-oxido)iron is monoclinic, space group  $P2_1/c$ ,  $Z = 4$ , with  $a = 7.997$  (4),  $b = 10.086$  (3),  $c = 13.534$  (4) Å;  $\beta = 124.64$  (4)°. Block-diagonal least-squares refinement of 1036 counter intensities led to a final  $R$  of 0.052. The coordination around Fe is a trigonal bipyramid. The apices are occupied by one carbonyl group [Fe—C = 1.762 (16) Å] and the O atom of the sulphoxide moiety [Fe—O = 2.064 (9) Å]. The equatorial plane contains the other two carbonyl groups [average Fe—C = 1.813 (12) Å] and the C=C double bond of the thiophene ring with average Fe—C = 2.036 (10) Å. The axial Fe—C(5) distance [1.762 (16) Å] is significantly shorter than the equatorial Fe—C(6) and Fe—C(7), 1.809 (12) and 1.817 (12) Å respectively.

### Introduction

As part of an investigation to improve the synthetic potential of the thiophene ring system by modifying the relative distribution of electron density in the ring, Eekhof, Hogeveen, Kellogg & Schudde (1976) synthesized an iron tricarbonyl complex of 2,5-dihydrothiophene 1-oxide. ESCA measurements suggested a complex bonding between the Fe and S atoms.

As no previous results of ESCA measurements on Fe tricarbonyl complexes were known, an X-ray determination was undertaken in order to establish the stereochemistry of the complex.

### References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 DE VRIES, G. F. & ADRIAN, H. W. W. (1975). *Proceedings of the Neutron Diffraction Conference, Petten 1975*, Report RCN-234, pp. 442–453.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.  
 SCHEUERMANN, W. & VAN TETS, A. (1977). *J. Raman Spectrosc.* To be published.  
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY 72 system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 VAN TETS, A. & ADRIAN, H. W. W. (1977). *J. Inorg. Nucl. Chem.* Submitted.

### Experimental

A sample was provided by Professor H. Hogeveen. The block-shaped orange-brown crystals (m.p. 78.5–79.5°C) had been obtained from ether–pentane at –25°C. The compound is stable at 0°C under nitrogen, and can be kept at room temperature for a few days in a nitrogen atmosphere. A suitable crystal was mounted in a Lindemann capillary under nitrogen. Space group, cell dimensions and intensities were obtained from measurements at approximately 0°C on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å).

### Crystal data

Molecular formula  $\text{C}_7\text{H}_6\text{O}_4\text{SFe}$ ;  $M_r = 242.03$ ; monoclinic,  $P2_1/c$ ,  $a = 7.997$  (4),  $b = 10.086$  (3),  $c =$

\* Author to whom correspondence should be addressed.

13.534 (4) Å;  $\beta = 124.64$  (4)°;  $V = 898.1$  Å<sup>3</sup>;  $D_c = 1.790$ ,  $D_o = 1.8$  g cm<sup>-3</sup>;  $F(000) = 488$ . Systematic absences:  $h0l$  with  $l = 2n + 1$ ,  $0k0$  with  $k = 2n + 1$ . The  $\omega$ -scan mode was used to record the intensities. A hemisphere of the reciprocal lattice was scanned up to  $\theta = 27.5^\circ$ ; averaging gave 1407 independent reflexions, of which 1036 with  $I > 2.5\sigma(I)$  were used in the structure determination.

No correction for absorption ( $\mu = 19.4$  cm<sup>-1</sup>) was applied. The dimensions of the crystal were  $0.20 \times 0.19 \times 0.11$  mm. The density was determined by flotation in a mixture of CHBr<sub>3</sub> and CCl<sub>4</sub>. The reference reflexions 021 and  $\bar{1}1\bar{1}$  were monitored every 25 reflexions. Fluctuations were within 4% of the mean values. There was no indication of decay during the measurement.

### Determination and refinement of the structure

In an  $E$  map, based on the most probable phase set for 240  $E$  values (*MULTAN*), the Fe and S atoms were located. The other non-hydrogen atoms were found by Fourier methods. Anisotropic least-squares refinement led to  $R_F = 0.062$ . The H atoms were found from a difference synthesis. Their temperature factors were fixed at  $2.2$  Å<sup>2</sup>. During further block-diagonal refinement the positional parameters of all atoms and the anisotropic parameters of the non-hydrogen atoms were varied. The refinement was considered to be complete when the shifts were within the estimated standard deviations; the resulting  $R_F$  is 0.052 and  $R_{wF}$  is 0.065. Unit weights were applied. In the final

Table 1. Final fractional coordinates ( $\times 10^4$ ; for H  $\times 10^3$ )

The estimated standard deviations in the least significant figures are given in parentheses here and in other tables.

|                     | <i>x</i>   | <i>y</i>   | <i>z</i>  |
|---------------------|------------|------------|-----------|
| Fe                  | 1818 (2)   | 8351 (1)   | 2193 (1)  |
| S                   | 5397 (4)   | 9804 (3)   | 2639 (3)  |
| O(1)                | 4677 (10)  | 8374 (7)   | 2526 (7)  |
| O(2)                | -2228 (12) | 8525 (9)   | 1659 (9)  |
| O(3)                | 3267 (13)  | 6671 (9)   | 4319 (8)  |
| O(4)                | 168 (14)   | 6677 (8)   | 41 (8)    |
| C(1)                | 3163 (17)  | 10532 (10) | 1351 (9)  |
| C(2)                | 1619 (15)  | 10253 (9)  | 1631 (9)  |
| C(3)                | 2478 (16)  | 10225 (9)  | 2872 (10) |
| C(4)                | 4738 (16)  | 10496 (10) | 3600 (9)  |
| C(5)                | -639 (18)  | 8448 (10)  | 1880 (11) |
| C(6)                | 2762 (16)  | 7304 (10)  | 3493 (10) |
| C(7)                | 873 (16)   | 7316 (11)  | 877 (10)  |
| H(C <sub>1</sub> )  | 348 (11)   | 1153 (8)   | 133 (7)   |
| H'(C <sub>1</sub> ) | 287 (13)   | 1006 (9)   | 65 (8)    |
| H(C <sub>2</sub> )  | 31 (12)    | 1065 (8)   | 116 (7)   |
| H(C <sub>3</sub> )  | 202 (10)   | 1049 (7)   | 329 (6)   |
| H(C <sub>4</sub> )  | 508 (21)   | 1154 (15)  | 382 (12)  |
| H'(C <sub>4</sub> ) | 533 (14)   | 1013 (10)  | 440 (8)   |

difference map no significant density was observed except for two diametrical peaks at 0.7 Å from the Fe atom, with a density of about  $1 e \text{ \AA}^{-3}$ . This may be attributed to the omission of absorption corrections. The scattering factors for C and O were from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965) and for Fe from *International Tables for X-ray Crystallography* (1962). The corrections for anomalous scattering for Fe were  $\Delta f' = 0.301$  and  $\Delta f'' = 0.845$  (Rietveld, 1966). The final positional parameters are presented in Table 1.\* All calculations were performed with an extended version of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a CDC Cyber-73 computer at the University of Utrecht.

### Description and discussion of the structure

The structure consists of monomeric molecules held together by van der Waals forces. All intermolecular distances shorter than 3.5 Å are shown in Fig. 1. Bond distances and angles are collected in Tables 2 and 3. The numbering scheme and the thermal vibrational ellipsoids are shown in Fig. 2 (*ORTEP*, Johnson, 1970).

The Fe atom is surrounded by five ligands. Because of the presence of strongly  $\pi$ -bonding carbonyl groups, the complex, as expected, adopts the trigonal bipyramidal configuration (Kettle, 1969). The equatorial plane of the trigonal bipyramid contains Fe, C(6), C(7) and also C(2) and C(3), which constitute one ligand. The equation of the plane is  $7.865X - 0.515Y - 5.638Z + 0.193 = 0$ , and the maximum deviation from it is  $-0.043$  Å for Fe. The plane through the Fe, S and the axial ligands O(1) and C(5)—O(2), with equation  $1.506X + 0.173Y - 12.382Z + 2.284 = 0$ , is approximately the mirror plane of the molecule. The angle between this plane and the equatorial plane is  $89.2^\circ$ .

The equatorial Fe—C(6) and Fe—C(7) lengths are 1.809 (12) and 1.817 (12) Å respectively; the axial Fe—C(5) bond, opposite to O(1), has a length 1.762 (16) Å while the Fe—O(1) distance is 2.064 (9) Å. These bond distances can be compared with the values 1.818 (17), 1.830 (16), 1.767 (20) and 2.004 (10) Å, respectively, in the butadieneirontricarboxyl-sulphur dioxide-boron trifluoride adduct (Churchill & Wormald, 1970) and 1.828 (8), 1.840 (9), 1.787 (8) and 1.995 (5) Å, respectively, in tricarbonyl-(1- $\eta$ -hexen-5-one)iron hexafluorophosphate (Hardy & Sim, 1972). Our Fe—O(1) distance is slightly longer

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32602 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

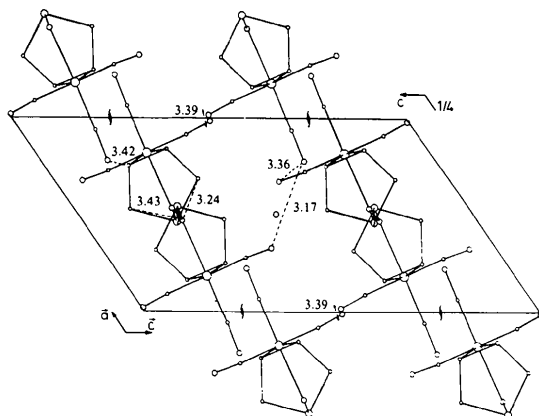


Fig. 1. Packing of  $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_6\text{OS})$  molecules within the unit cell as viewed along *b*.

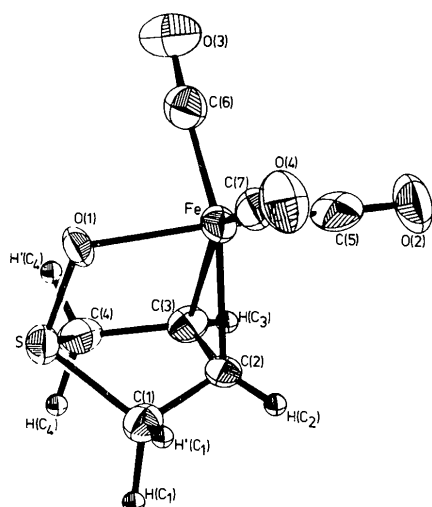


Fig. 2. The 50% probability ellipsoids for  $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_6\text{OS})$ . The numbering scheme is indicated.

than those mentioned above. This may be attributed to the resistance of 2,5-dihydrothiophene 1-oxide to the distortion of the ring necessary to bring the O(1) ligand into a bonding position. This distortion reduces the angle between the plane through C(1), C(2), C(3), C(4) and the plane through S, C(1), C(4) from  $180^\circ$ , as in the non-distorted molecule 2,5-dihydrothiophene 1,1-dioxide (Sands & Day, 1967), to  $134.2^\circ$  in our structure.

The axial Fe—C(5) distance [1.762 (16) Å] is short compared with the axial Fe—C bonds, 2.00 (1) and 1.98 (1) Å, in tetracarbonyl(acrylonitrile)iron (Luxmoore & Truter, 1962). This contraction is explained by the absence of back-donation of  $\pi$ -electron charge from Fe to the O(1) ligand of the sulphoxide moiety, the Fe—O(1) distance of 2.064 (9) Å being indicative of an essentially single bond (Hardy & Sim, 1972). The other intramolecular distances are normal.

Table 2. Bond distances (Å) within the tricarbonyl(2,5-dihydrothiophene 1-oxido)iron molecule

|           |            |                          |            |
|-----------|------------|--------------------------|------------|
| Fe—O(1)   | 2.064 (9)  | Fe—C(5)                  | 1.762 (16) |
| Fe—C(2)   | 2.037 (10) | Fe—C(6)                  | 1.809 (12) |
| Fe—C(3)   | 2.036 (10) | Fe—C(7)                  | 1.817 (12) |
| C(1)—C(2) | 1.509 (22) | C(1)—H(C <sub>1</sub> )  | 1.04 (8)   |
| C(2)—C(3) | 1.409 (17) | C(1)—H'(C <sub>1</sub> ) | 0.97 (11)  |
| C(3)—C(4) | 1.513 (16) | C(2)—H(C <sub>2</sub> )  | 0.95 (8)   |
| S—C(1)    | 1.797 (9)  | C(3)—H(C <sub>3</sub> )  | 0.87 (11)  |
| S—C(4)    | 1.799 (16) | C(4)—H(C <sub>4</sub> )  | 1.08 (15)  |
| S—O(1)    | 1.528 (8)  | C(4)—H'(C <sub>4</sub> ) | 0.98 (10)  |
| C(5)—O(2) | 1.131 (19) | C(7)—O(4)                | 1.135 (14) |
| C(6)—O(3) | 1.143 (16) |                          |            |

Table 3. Bond angles ( $^\circ$ ) in the molecule tricarbonyl(2,5-dihydrothiophene 1-oxido)iron

|                |            |              |            |
|----------------|------------|--------------|------------|
| O(1)—Fe—C(2)   | 85.0 (4)   | C(2)—Fe—C(7) | 105.9 (5)  |
| O(1)—Fe—C(3)   | 85.5 (4)   | C(3)—Fe—C(5) | 91.4 (5)   |
| O(1)—Fe—C(5)   | 176.0 (4)  | C(3)—Fe—C(6) | 104.1 (5)  |
| O(1)—Fe—C(6)   | 89.8 (5)   | C(3)—Fe—C(7) | 146.4 (5)  |
| O(1)—Fe—C(7)   | 90.7 (5)   | C(5)—Fe—C(6) | 93.3 (6)   |
| C(2)—Fe—C(3)   | 40.5 (5)   | C(5)—Fe—C(7) | 90.6 (6)   |
| C(2)—Fe—C(5)   | 91.0 (5)   | C(6)—Fe—C(7) | 109.2 (5)  |
| C(2)—Fe—C(6)   | 144.5 (5)  |              |            |
| C(1)—C(2)—C(3) | 112.9 (9)  | C(4)—S—O(1)  | 100.9 (6)  |
| C(2)—C(3)—C(4) | 111.4 (13) | S—O(1)—Fe    | 109.9 (4)  |
| C(3)—C(4)—S    | 101.0 (8)  | C(1)—C(2)—Fe | 111.6 (7)  |
| C(4)—S—C(1)    | 90.3 (6)   | C(3)—C(2)—Fe | 69.7 (6)   |
| S—C(1)—C(2)    | 100.6 (8)  | C(2)—C(3)—Fe | 69.8 (6)   |
| C(1)—S—O(1)    | 100.3 (4)  | C(4)—C(3)—Fe | 111.6 (8)  |
| Fe—C(5)—O(2)   | 178.6 (12) | Fe—C(7)—O(4) | 175.8 (13) |
| Fe—C(6)—O(3)   | 176.0 (14) |              |            |

The data were collected by Dr A. J. M. Duisenberg. Part of this work (ALS) was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Advancement of Pure Research (ZWO).

## References

- CHURCHILL, M. R. & WORMALD, J. (1970). *Inorg. Chem.* **9**, 2430–2436.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- EKKHOF, J. H., HOGVEEN, H., KELLOGG, R. M. & SCHUDDE, E. P. (1976). *J. Organomet. Chem.* **105**, C35–C38.
- HARDY, A. D. U. & SIM, G. A. (1972). *J. Chem. Soc. Dalton*, pp. 2305–2308.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KETTLE, S. F. A. (1969). *Coordination Compounds; Studies in Modern Chemistry*. London: Thomas Nelson.

LUXMOORE, A. R. & TRUTER, M. R. (1962). *Acta Cryst.* **15**, 1117–1124.  
 RIETVELD, H. M. (1966). *Fysica Memo* 153. RCN Petten, The Netherlands.  
 SANDS, D. E. & DAY, V. W. (1967). *Z. Kristallogr.* **124**, 220–227.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

*Acta Cryst.* (1977). **B33**, 3003–3005

## The Crystal Structure of Methyl $\beta$ -D-Galactopyranoside

BY B. SHELDRIK

*Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, England*

(Received 17 February 1977; accepted 18 March 1977)

The structure of methyl  $\beta$ -D-galactopyranoside has been determined by direct methods. Refinement was by full-matrix least squares with anisotropic temperature factors for the C and O atoms to produce a final  $R$  of 0.040 for 917 measured reflexions. The space group is  $P2_12_12_1$  with  $Z = 4$ ,  $a = 7.7784$  (3),  $b = 8.5335$  (6),  $c = 13.1315$  (5) Å. The configuration is  $1e2e3e4a$  and hydrogen bonds are formed by each hydroxyl group but the ring O does not act as an acceptor.

### Experimental

Cell dimensions and systematic absences ( $h00$  for  $h = 2n + 1$ ,  $0k0$  for  $k = 2n + 1$  and  $00l$  for  $l = 2n + 1$ ) were established from Weissenberg photographs and the cell dimensions refined by least squares from  $2\theta$  measurements of 70 reflexions at room temperature with Cu  $K\alpha$  radiation on a diffractometer.

### Crystal data

$C_7O_6H_{14}$ , FW 194.19, space group  $P2_12_12_1$ ,  $a = 7.7784$  (3),  $b = 8.5335$  (6),  $c = 13.1315$  (5) Å,  $V = 871.6$  Å<sup>3</sup>,  $D_x = 1.48$  g cm<sup>-3</sup> for  $Z = 4$ , Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å, crystal size:  $0.11 \times 0.17 \times 0.31$  mm, crystal shape: prism. Crystallized from 1:10 water:propan-1-ol.

Intensities were collected on an Enraf–Nonius CAD-4 diffractometer in the range  $3^\circ < \theta \leq 70^\circ$ , scanned in the  $\omega$ - $2\theta$  mode. 917 independent reflexions were measured and 34 more were too weak. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) to give the positions of all the non-hydrogen atoms. Refinement with isotropic temperature factors reduced  $R$  to 0.166 and with anisotropic factors to 0.084. The positions of the H atoms were established from a difference synthesis and included in the refinement with isotropic temperature factors fixed at the average of the atom to which they are bonded. The final  $R$  for the 917

independent measured reflexions is 0.040, and including 34 weak reflexions at one half of the minimum measured intensity  $R$  is 0.046. The refinement and

Table 1. Fractional atom coordinates ( $\times 10^5$ ) and e.s.d.'s in parentheses

|       | <i>x</i>     | <i>y</i>    | <i>z</i>    |
|-------|--------------|-------------|-------------|
| C(1)  | 16140 (49)   | 46298 (42)  | 58422 (25)  |
| C(2)  | 2010 (47)    | 34139 (45)  | 57656 (26)  |
| C(3)  | 1600 (46)    | 24583 (45)  | 67399 (26)  |
| C(4)  | 19234 (44)   | 17804 (40)  | 69986 (24)  |
| C(5)  | 32494 (47)   | 31055 (41)  | 70033 (25)  |
| C(6)  | 50400 (51)   | 24992 (46)  | 72073 (32)  |
| C(7)  | 27503 (83)   | 68287 (57)  | 49717 (41)  |
| O(1)  | 17819 (40)   | 54011 (31)  | 49052 (18)  |
| O(2)  | -14296 (34)  | 41925 (36)  | 56803 (19)  |
| O(3)  | -11048 (38)  | 12535 (39)  | 67036 (21)  |
| O(4)  | 23664 (34)   | 5979 (28)   | 62754 (18)  |
| O(5)  | 32491 (32)   | 38532 (30)  | 60268 (17)  |
| O(6)  | 62233 (35)   | 37724 (37)  | 72888 (21)  |
| H(1)  | 13298 (591)  | 53486 (526) | 64697 (313) |
| H(2)  | 3482 (574)   | 26354 (573) | 51222 (360) |
| H(3)  | -787 (663)   | 32164 (615) | 72981 (347) |
| H(4)  | 18383 (589)  | 11967 (566) | 76898 (319) |
| H(5)  | 28974 (571)  | 40535 (539) | 75472 (308) |
| H(6)  | 54114 (582)  | 17517 (582) | 66034 (337) |
| H(7)  | 50781 (617)  | 17743 (562) | 78386 (354) |
| H(8)  | -16458 (688) | 40476 (593) | 51010 (372) |
| H(9)  | -11964 (748) | 9444 (678)  | 61828 (368) |
| H(10) | 28205 (633)  | -1020 (608) | 65700 (345) |
| H(11) | 66860 (659)  | 38700 (639) | 68049 (349) |
| H(12) | 26211 (761)  | 73784 (675) | 43855 (476) |
| H(13) | 23664 (804)  | 74361 (691) | 54587 (480) |
| H(14) | 40965 (774)  | 67071 (638) | 52938 (435) |